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**Den Norske Stats Oljeselskap AS, Postboks 300, Forus,
4001 Stavanger, NO.**

Inventor:

Bjørn Vassøy, Stavanger, NO

Method for the addition of silicon oxide to a hydraulic cement slurry.

Abstract

A method for the addition of silicon oxide to a hydraulic cement slurry,
particularly for well cementing, characterized in that

- amorphous silica having a particle size of less than 1 micrometers is mixed with water to liquid microsilica,
- silica powder having a particle size of from 2 to 200 micrometer is mixed with the liquid microsilica,
- the silica mixture thus obtained is added to the cement slurry directly in a mixing tank.

Hydraulic cement slurry containing

hydraulic cement, 5 – 100% silicon oxide additive containing liquid amorphous silica having a particle size of less than 1 micrometer and added silica powder based on the weight of cement, 2 – 200% light-weight aggregate having a true particle density of between 0.1 and 1.5 g/cm³, based on the weight of cement, 0 – 5% thinner (dry weight) based on the weight of cement, 1 – 10% filter loss reducing agent (dry weight) based on the weight of cement, and water in an amount such that the cement slurry has a density of between 0.8 and 2.0 g/cm³.

The present invention relates to a method for adding silicon oxide to a hydraulic cement slurry, particularly for well cementing.

Hydraulic cement slurries of this type are used primarily in hydrocarbon wells and in geothermic wells.

Cement slurries into which silicon oxide is mixed are typically used in oil well cement where the primary purpose is to prevent strength reduction in the cement slurry over time, particularly at high pressure and at temperatures exceeding 100°C.

In primary cementing of hydrocarbon wells the cement slurry is pumped down through a casing in the well, and up on the outside, such that it fills the annulus between the casing and the borehole wall. The most important objectives in the cementing are:

- 1) To support and protect the casing.
- 2) To isolate weak structures or high pressure zones.
- 3) To prevent water, oil or gas from moving between structures or up to the surface.

The current technology

A common cement mixture used in hydrocarbon wells, when exposed to temperatures above 100 °C for some length of time, will gradually lose compression strength at the same time as the permeability increases. These qualities are augmented with increasing temperature.

At temperatures above 130 °C, this can occur already after 24 hours. It can go to the extent that the cement crumbles up and thus loses its functionality.

At temperatures above 100 °C, the usual C-S-H-(calcium-silicate-hydrate) bond is converted to alpha-calcium-silicate-hydrate. The strength is hereby reduced, and the permeability increases.

To prevent this reaction it is customary procedure to add SiO₂, silicon oxide, to the cement slurries. SiO₂ prevents the formation of alpha-calcium-silicate-hydrate. Instead there is formed mono-calcium-silicate-hydrate, which is a more stable bond. The strength is thereby maintained. The most common way of supplying SiO₂ to the

cement slurries is to add silica powder or silica sand. Both substances consist mainly of SiO_2 .

Silica powder is a light gray/white powder produced from quartz. It is produced both in Europe and in the USA and has a number of product names such as "SSA-1" from Halliburton Services, "D-66" from Dowell Schlumberger or "D-8" from B.J. Hughes. The specific weight is about 2.63 gcm^{-3} . The grain size lies between 2 and 200 micrometers, about 50 % by weight is less than 50 micrometers. This is approximately the same grain size as in oil well cement.

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Silica sand is more coarse-grained than silica powder. The grain size is usually from 1 to 2 mm. Silica sand is also produced from quartz and also has a specific weight of about 2.63 gcm^{-3} .

15 Silica powder is absolutely the most used substance. To prevent strength reduction in the cement mixture, one must use a minimum of 35% silica powder based on the weight of cement.

Today this silica powder is dry mixed with the dry cement in silos on land. This is done by blowing each dry substance with compressed air from each respective silo into a third silo. Then the mixture is blown back and forth between two silos. This results in an approximately homogeneous mixture. These blowing procedures, however, are detrimental to the properties of the cement in the finished cement slurry due to the fact that the compressed air contains small amounts of water. The qualities that are 25 impaired are: free water is increased, the filter loss increases and solidification time is increased. These properties are all critical for a cement slurry.

With this mixing method it is very difficult to achieve a precise proportioning of the various components. This is because the measuring of exact amounts of dry substances is a technically difficult process. Moreover, there are difficulties involved in 30 attaining a homogeneous and stable mixture.

The current art also requires that the rigs be provided with their own storage silos for the storage of the dry mixture. In many cases, this can result in problems due to poor silo capacity. Moreover, there is blended so much of the dry mixture that there is 35 enough for two jobs (100% back-up). What is left over after the completion of the cementing job is most often used in cement slurries where it is not necessary to utilize

silica powder. This is done in order to dispose of the mixture so that space in the storage silo is freed for conventional cement. This is economically rather unfavorable.

Recently it has become apparent that by the addition of microsilica it is also possible to prevent strength reduction at high temperatures. Microsilica reacts in the same way as silica powder in a cement mixture exposed to high temperatures. Here, also, mono-calcium-silicate-hydrate is formed.

As microsilica there is preferably used silica dust collected from electro thermal melting furnaces that produce at least 75% ferrosilicon (Si content of at least 76%), but dust from furnaces that produce 50% ferrosilicon can also be used as a starting material for the present invention.

It is also possible to obtain silica dust as a main product from the above-mentioned melting furnaces by adjusting the reduction conditions. Amorphous silica of this type can also be produced synthetically without reduction and reoxidation. Alternatively a silica dust generator can be used to produce comminuted silica, or silica can be produced by precipitation.

To render the microsilica readily transportable it is mixed by the manufacturer with about 50% by weight of fresh water. There is thus obtained a liquid microsilica having a specific weight of about 1.40 gcm^{-3} . Elkem, for example, has given this mixture the product name "EMSAC 460S."

In order to be able to add a sufficient amount of liquid microsilica, it is necessary to reduce the density of the cement slurry, by a known method, from about 1.90 gcc to about 1.70 gcc.

Then the mixture must be weighted up again to the desired density by means of weighting materials. This is a cumbersome solution, but even more serious is the fact that this method produces an excessively viscous and thixotropic cement slurry.

By another known method, one increases the pH of the mixture before all the cement is added, in order to manage to incorporate 35 % microsilica. Thus the tiny microsilica particles are flocculated, and this produces a slurry that is not gas-tight. Moreover, this method also yields an excessively viscous and thixotropic cement slurry.

The objective of the present invention is to provide an improved method for the addition of silicon oxide where the above-mentioned problems are overcome.

The present invention

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This is achieved according to the present invention by a method that is characterized in that:

- amorphous silica having a particle size of less than 1 micrometer is mixed with water to liquid microsilica,
- 10 - silica powder having a particle size of from 2 to 200 micrometers is mixed into the liquid microsilica and the silica mixture thus obtained is added to a cement slurry directly in a mixing tank.

Amorphous silica dust that is used in the present invention consists primarily of
15 submicron spherical particles.

The silica dust particles may, for example, contain 60 – 100% by weight of SiO_2 and have a density of $2.0 - 2.40 \text{ g/cm}^3$ and a specific surface area of $15 - 30 \text{ m}^2/\text{g}$. The particles are mainly spherical and have a particle size of less than 1 micrometer.
20 Variations in these values are, of course, possible. For example, the silica dust may have a lower SiO_2 content and the particle size distribution may be adjusted, for example, by removing larger particles.

Silica powder and liquid microsilica are mixed such that the sum of the two substances
25 constitutes a minimum of 35% by weight dry substance of dry cement weight in a cement slurry. The strength reduction at high temperature is hereby prevented. The mixture of the two substances also provides the cement slurries with very good properties, such as very low viscosity, minimal thixotropic properties, stable slurries, low filter loss and no free water. Moreover the slurries that contain more than a given
30 amount of microsilica have gas-tight properties.

The mixture of the two substances can be done on land in an agitator. Since liquid microsilica is one of the components, it is capable of being measured with great accuracy. The silica powder is added to the liquid microsilica until the desired density
35 of the finished mixture is attained. One obtains a mixture having a precise composition.

Other advantages of the invention:

- 5 - The mixture is completely stable even on several months' storage.
- The mixture is readily pumpable and can be added directly in a mixing tank on the rig or directly in the mixing tanks on cement mixing units.
- Extra blowing operations of dry cement and silica powder from one silo to another are avoided.
- 10 - The mixture does not require special storage tanks on the rigs.
- Excess amounts of the mixture can be returned to land and stored for later use.

The invention will now be described in more detail with the aid of the following examples.

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Example 1

A silica mixture was produced having the following composition:

20 Silica powder, "SSA-1"	55.6 weight percentage
Microsilica (50% dry substance)	44.4 weight percentage

The silica powder is "SSA-1" supplied by Halliburton Services, Tananger. Microsilica is "EMSAC 460S" from Elkem, Bremanger Smelteverk (50 weight percentage dry
25 substance in water).

Rheological properties at 20°C were:

600 rpm = 210 cp, 300 rpm = 126 cp, 200 rpm = 94 cp, 100 rpm = 53 cp.

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The mixture of silica powder and liquid microsilica may contain 5-80 weight percentage silica powder, preferably 40-60 weight percentage, and 20-95 weight percentage liquid microsilica, preferably 40-60 weight percentage.

35 In addition, to mixtures of silica powder in liquid microsilica there may also be added all types of weighting materials, dispersing agents, retarders, accelerators, filter loss reducing substances, weight reducing substances and anti-foaming agents.

As weighting materials there may be used all the types that are used in oil well cement, preferably hematite, ilmenite or barite. The mixture may conceivably also contain 0-50% by weight of weighting material, preferably 0-20% by weight.

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As dispersants there may be used such agents as are known to be used as plasticizing – or superplasticizing – agents in cement based systems: for example, agents based on lignosulfonates, partially desulfonated lignosulfonates, polyhydroxyl carboxylic acids, sulfonated naphthalene-formaldehyde – or sulfonated melamine-formaldehyde products.

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The mixture may conceivably contain 0-10% by weight of dispersing agent (based on dry substance), preferably 0-2% by weight.

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The mixture may contain retarders such as cellulose derivatives, sugar derivatives, lignosulfonates and lignins.

The mixture may conceivably contain 0-10% by weight of retarder based on dry substance, preferably 0-2% by weight.

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As accelerator there may be used sodium chloride (NaCl) and calcium chloride (CaCl₂).

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The mixture may conceivably contain 0-10% by weight of accelerator, preferably 0-2% by weight.

The mixture may contain filter loss reducing agents, e.g., agents based on starch or amyl derivatives, cellulose derivatives such as carboxymethylcellulose, methylcellulose or ethylcellulose, or synthetic polymers such as, e.g., polyacrylonitrile or polyacrylamide.

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The mixture may conceivably contain 0-10% by weight of filter loss reducing agent (based on dry weight), preferably 0-2% by weight.

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As weight reducing substances it is particularly preferred to use hollow glass spheres. This type of lightweight aggregate is available under a number of product names, e.g., hollow glass spheres produced by 3M Company, USA.

Also hollow spheres obtained from fuel ash can conceivably be used, for example, the product "Fillite" that is produced by Fillite Ltd., England.

- 5 The mixture may conceivably contain 0-50% by weight of weight reducing substances, preferably 0-30% by weight.

As water there may be used, according to the present invention, fresh water or sea water. The mixture may conceivably contain 0-50% by weight of water, preferably 0-
10 20% by weight.

The mixture can be used in cement slurries based on all types of oil well cement described in API SPEC 10.

15 Example 2

A typical cement slurry which incorporates the silicon oxide mixture described above in this example is:

20	Norcem G-cement	100 kg
	Silica powder	25 kg
	Microsilica, 50% dry substance	20 kg
	Filter loss reducing agent	7 l
	Dispersing agent	0.5 kg
25	Retarder	0.97 kg
	Fresh water	36.59 l

This cement slurry had the following characteristics:

30	Density:	1.90 g/cm ³
	Silica powder, "SSA-1"	55.6 weight percentage
	Microsilica (50% dry substance)	44.4 weight percentage

- 35 Plastic viscosity was 84 cp, and yield point was 20.16 Pa.

Rheological properties at 90°C:

300 rpm: 23 cp, 200 rpm: 17 cp, 100 rpm: 10 cp, 6 rpm: 1 cp.

API SPEC 10 filter loss: 34 cm³/30 min.

5 Compression strength after 24 hours at 124°C: 216 bars.

Example 3

10 To compare the compression strength of a cement slurry containing the silicon oxide mixture with a slurry in accordance with the known art, one can refer to two cement slurries 1 and 2 having the following compositions:

Slurry 1: (in accordance with the known art)

15	G-cement	100.0 kg
	Liquid microsilica	11.0 kg
	Filter loss reducing substance	0.5 kg
	Dispersing agent	3.0 l
	Retarder	0.27 l
20	Anti-foaming agent	0.20 l
	Fresh water	36.40 l

Density of the slurry: 1.90 g/cm³.

25 Slurry 2: (where the invention is incorporated)

	G-cement	100.0 kg
	Silica powder	25.0 kg
	Liquid microsilica (50% dry substance)	41.7 kg
30	Filter loss reducing substance	10 l
	Dispersing agent	0.5 kg
	Retarder	0.4 kg
	Anti-foaming agent	0.2 l
	Fresh water	78.86 l

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Density of the slurry: 1.60 g/cm³.

The development of the compression strength over time at 134°C was measured with an "Ultrasonic Cement Analyzer" (UCA), and the results are given in the table below:

Slurry No.	UCA compression strength at 134°C (bar)							
	0.5 day	1 day	2 days	3 days	5 days	7 days	14 days	28 days
1	145	155	152	138	117	103	56	-
2	55	93	103	105	107	110	110	110

Slurry no. 2 attains a lower compression strength than no. 1, initially because of lower specific weight for the slurry.

P a t e n t C l a i m s

1. A method for the addition of silicon oxide to a hydraulic cement slurry, particularly for well cementing, characterized in that
 - 5 - amorphous silica having a particle size of less than 1 micrometer is mixed with water to liquid microsilica,
 - silica powder having a particle size of from 2 to 200 micrometers is mixed with the liquid microsilica,
 - the silica mixture thus obtained is added to the cement slurry directly in a mixing
10 tank.
2. A method according to claim 1, characterized in that there is added a silica mixture containing from 5 to 80 weight percentage silica powder, preferably from 40 to 60 weight percentage, and from 95 to 20 weight percentage liquid
15 microsilica, preferably from 60 to 40 weight percentage based on the weight of dry substances, and to the mixture there is in addition added from 0 to 50 weight percentage water, preferably below 20 weight percentage based on the weight of dry substances, where the water may be fresh water or sea water.
- 20 3. A method according to claim 1 or 2, characterized in that the silica powder and microsilica together constitute a minimum of 35 weight percentage of the cement on the basis of dry substances in a cement slurry.

